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MENKE'S METHOD OF PREPARING HYPONITRITES.

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Hyponitrites were first prepared in 1871 by Edward Divers* by reducing an alkaline nitrate in water solution by means of sodium amalgam. About seven years later A. E. Menke†, of Kings College, London, obtained a compound by heating cast iron filings with sodium nitrate which Professor Bloxam suggested to be the compound discovered by Dr. Divers. An analysis of the sodium determined as sodium sulphate and an analysis of the nitrogen determined as ammonia yielded the theoretical amounts of these elements, all within the limits of experimental error. On drying at 100° C. it lost in weight corresponding to three molecules of water of crystallization. He also prepared the silver salt and analyzed it, and the results corresponded to theory.

Some time since, while engaged in the study of "hyponitrites", I endeavored to prepare sodium hyponitrite by Menke's method. It appealed to me as being the cheapest and most convenient, and as one that would give a large yield. I obtained a crystalline, fluorescent salt which, when dried at 100° C. lost in weight corresponding to four molecules of water of crystallization. It yielded on analysis the theoretical amount of sodium in sodium hyponitrite. When a water solution was treated with a solution of silver nitrate, it yielded a precipitate which had the appearance of the silver salt of hyponitrous acid described by Dr. Divers. On analysis it yielded the theoretical amount of silver in silver hyponitrite. On treating the

*Journal of the London Chemical Society, 1871, 484.
†Journal of the London Chemical Society, 1878, Transactions, 401.

sodium salt with an acid, however, it did not evolve nitrous oxide but carbon dioxide. It did not yield nitrogen by any of the common qualitative tests. I also attempted to determine the amount of nitrogen by the absolute method but found none. The salt obtained was therefore a carbonate. The fact that the sodium and the silver, obtained by the analysis of the respective salts, correspond to both carbonate and hyponitrite, is explained by the fact that hyponitrous acid and carbonic acid have the same molecular weight.

$$H_2N_2O_2 = 2 + 28 + 32 = 62.$$
$$H_2CO_3 = 2 + 12 + 48 = 62.$$

I endeavored to prepare sodium hyponitrite by this method repeatedly, varying the conditions each time, but always with the same result.

In view of the above experiments there are several other reasons that would lead one to suspect that Menke obtained sodium carbonate instead of sodium hyponitrite.

First.—Like sodium carbonate, Menke's salt was an efflorescent substance. It contained six molecules of water of crystallization (using the double formula), but sodium carbonate, under varying conditions, crystallizes out with one, two, five, six, seven, ten or fifteen molecules of water.

Second.—Menke obtained the best yield by keeping the crucible at a red heat for an hour after deflagration ensued. This might be explained on the ground that it would give more time for the oxidation of the carbon in the iron, which exists very largely as graphite and which is completely oxidized to carbon dioxide only by long continued heating with sodium nitrate. A great deal of carbonate must have been formed during the process, especially in view of the fact that cast iron was used, which contains from 2 to 5 per cent of carbon. The carbon in uniting with sodium and oxygen would produce nearly nine fold its own weight of sodium carbonate, or for every 100 grams of iron employed there would be produced from eighteen to forty-five grams of sodium carbonate, providing there was sufficient sodium to combine with it. While there would

be only one-half the amount of sodium present to produce this much carbonate, and in practice there would be much less produced than theory would indicate, there must still have been a large amount of this salt to deal with.

Alkaline nitrites have the power of absorbing carbon dioxide and giving off oxides of nitrogen, thus changing spontaneously into carbonates when conditions are favorable. It is also well known that nitrates are changed into nitrites by the action of many reducing agents. In the light of the above, then, the first step would probably be the changing of the nitrate to nitrite by the reducing action of the iron. In the second step the carbon dioxide which has been formed replaces the "N_2O_3" in two molecules of sodium nitrite.

Third.—The precipitates which Menke's sodium salt yielded with various salts of the heavy metals are quite different from those described by Divers, and quite identical with those yielded by a solution of sodium carbonate.

DIVER'S HYPONITRITE.

Copper sulphate gives a yellowish, olive green precipitate.

Lead acetate gives a cream white, floculent precipitate.

Mercuric chloride gives a cream white floculent precipitate.

Mercurous nitrate gives a blackish, gray precipitate.

Nickel chloride gives a greenish, almost white, precipitate.

Manganese chloride gives a nearly white precipitate.

Ferric chloride gives a reddish-brown precipitate.

Ferrous sulphate gives a whitish precipitate which instantly changes to a dirty, blackish green.

Zinc chloride gives a white precipitate.

Barium chloride gives no precipitate.

MENKE'S "HYPONITRITE."

Copper sulphate gives a torquois blue precipitate.

Lead acetate gives a white precipitate.

Mercuric chloride gives a white precipitate which becomes yellow and then brownish-red.

Mercurous nitrate gives a black precipitate.
Nickel sulphate gives a whitish-green precipitate.
Manganese chloride gives a white precipitate.
Ferric chloride gives a yellow precipitate.
Ferrous sulphate gives an olive green precipitate.
Zinc chloride gives a white precipitate.
Baryta gives a white precipitate.

SODIUM CARBONATE.

Copper sulphate gives a turquois blue precipitate.
Lead acetate gives a white precipitate.
Mercuric chloride gives a light yellow precipitate which turns brownish red.
Nickel sulphate gives a whitish green precipitate.
Manganese chloride gives a white precipitate.
Ferric chloride gives a brown precipitate.
Ferrous sulphate gives an olive green precipitate.
Zinc chloride gives a white precipitate,
Barium chloride gives a white precipitate.

It will be observed that the only essential difference in the precipitates yielded by "Menke's hyponitrite" and sodium carbonate is in case of ferric chloride which yields a brown precipitate instead of a yellow one, and that might even be described as yellow in dilute solution.

We presume that Menke did his work under the eye of Professor Bloxam, and he did not seem to doubt it in any way. In his text-book on Inorganic and Organic Chemistry, page 145, he states that "the sodium salt may be prepared in large quantity by fusing sodium nitrate with iron filings in an iron crucible."

It may be said that other methods have failed in the hands of those who followed the discoverer. Zorn prepared alkaline hyponitrite by reducing nitrates with ferrous hydroxide, but for some years afterwards, those who followed him failed in their attempts to apply his method. Notwithstanding all that can be said in favor of Menke's method, while it is still possible, it would seem evident that he mistook sodium carbonate for sodium hyponitrite.